



Review article

Colloid-borne forms of tetravalent actinides: A brief review



Harald Zänker*, Christoph Hennig

Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, P.O. Box 51 01 19, D-01314 Dresden, Germany

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ABSTRACT

Tetravalent actinides, An(IV), are usually assumed to be little mobile in near-neutral environmental waters because of their low solubility. However, there are certain geochemical scenarios during which mobilization of An(IV) in a colloid-borne (waterborne) form cannot be ruled out. A compilation of colloid-borne forms of tetravalent actinides described so far for laboratory experiments together with several examples of An(IV) colloids observed in field experiments and real-world scenarios are given. They are intended to be a knowledge base and a tool for those who have to interpret actinide behavior under environmental conditions. Synthetic colloids containing structural An(IV) and synthetic colloids carrying adsorbed An(IV) are considered. Their behavior is compared with the behavior of An(IV) colloids observed after the intentional or unintentional release of actinides into the environment. A list of knowledge gaps as to the behavior of An(IV) colloids is provided and items which need further research are highlighted.

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* Corresponding author. Tel.: +49 351 260 3209; fax: +49 351 260 3553.

E-mail address: h.zaenker@hzdr.de (H. Zänker).

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1. Introduction

Due to their low solubility (cf. Altmaier et al., 2004; Neck and Kim, 2001; Neck et al., 2002; Opel et al., 2007; Rai et al., 1990; Rai et al., 1995), tetravalent actinides, An(IV), are usually assumed to be little mobile in natural waters. Reducing conditions, which tend to transform the actinides into their tetravalent form, are therefore often advantageous to oxidizing conditions with respect to actinide immobilization. Radionuclides such as ^{129}I , ^{36}Cl , ^{79}Se , ^{14}C or ^{99}Tc should be more mobile and, thus, more critical than actinides under such conditions (Grambow, 2008). However, there are several mechanisms which may mobilize actinides even in the tetravalent state.

Firstly, in alkaline solutions of high carbonate concentration tetravalent actinides are able to form readily soluble *carbonate complexes* and *hydroxo-carbonate complexes* (Altmaier et al., 2005; Bruno et al., 1989; Hennig et al., 2010; Östholts et al., 1994; Rai et al., 1995, 1998) and in calcium-containing alkaline solutions tetravalent actinides can form *calcium-An(IV) hydroxide complexes* which are soluble (Brendebach et al., 2007). Secondly, in slightly acidic sulfate solutions as those in uranium mines after the application of in situ uranium leaching soluble *uranium(IV) sulfate complexes* can be formed (Hennig et al., 2008). Thirdly, actinides can also be mobilized in undissolved forms as *colloids* (waterborne particles having at least one dimension in the range of 1 nm to 1 μm) which may take place within a broad pH range including the near-neutral range.

Actinide(IV) transport in the form of colloids is increasingly in the focus of research. Recently, Kersting (2013) stated that for plutonium, the actinide causing particular environmental hazard, there has been a paradigm shift in the understanding of environmental behavior over the last 10 to 15 years. Once thought to be greatly immobile in the subsurface because of the very low solubility and high surface reactivity of its tetravalent form, Pu has now been shown to migrate at low concentrations as plutonium(IV) colloids. Thorium(IV) and uranium(IV), too, have been identified to be mobile in colloidal forms (cf. Geckeis et al., 2004; Kalmykov et al., 2011). Indeed, in almost all cases where actinide(IV) transport has been reported for real environmental scenarios, there are strong indications that transport via colloids was the dominant transport mechanism (compare Section 4 below). Unfortunately, our general understanding of the colloid-facilitated transport of actinides is still limited. In particular, there are still no predictive numerical models which include colloid-facilitated transport of actinides in a satisfactory manner. This is true in spite of the remarkable amount of

research that has already been devoted to An(IV) colloids and the considerable body of literature on this subject already in existence (see e.g. Geckeis, 2004; Geckeis and Rabung, 2008; Honeyman, 1999; Kalmykov and Denecke, 2011; Kersting, 2013; Kim, 1991, 2006; Maher et al., 2013; Schäfer et al., 2012; Sen and Khilar, 2006; Silva and Nitsche, 1995; Walther and Denecke, 2013 and references in these reviews). The hitherto existing literature can be roughly divided into two groups:

- Publications on simplifying well-defined laboratory experiments with An(IV),
- Publications providing phenomenological descriptions of An(IV) transport in real-world scenarios.

Type (a) publications provide valuable information on the fundamentals of An(IV) colloid formation and behavior. However, their help in interpreting real environmental An(IV) transport scenarios is often limited because such scenarios are not well-defined but extremely complex and laboratory experiments take the processes out of context. Publications of type (b), on the other hand, provide more practice-oriented information, but this information is often hard to generalize and to model. It tends to be site-specific.

Here we give a compilation of colloid-borne forms of tetravalent actinides described so far, no matter if identified in laboratory experiments or real environmental scenarios. We are convinced that such a compilation can be a knowledge base and a tool for those who have to interpret actinide behavior in both laboratory experiments and real-world scenarios.

We do not go into details with respect to the various techniques of colloid investigation; such information we give elsewhere (Zänker, 2010; Zänker and Schierz, 2012). However, it is at least worth mentioning that one is faced with several difficulties and obstacles when investigating An(IV) colloids which are less often encountered when dealing with other systems. Such difficulties are:

- Some of the actinides require cumbersome precautions to maintain them in the tetravalent state.
- Plutonium, in particular, is able to coexist in several oxidation states in the same solution which makes controlling chemistry difficult.
- Colloid and/or precipitate formation is preceded by a series of hydrolysis steps of dissolved hydroxo complexes which all must be known and taken into consideration in the quantitative assessment of results.

- (iv) The dissolved hydrolysis products, polymers and colloids of tetravalent actinides tend to adsorb onto the walls of the reaction vessels which may perturb or even ruin the experiments.

2. The problem of colloid-facilitated actinide(IV) transport

2.1. Actinide chemistry

Potential sources of actinides in the biosphere are uranium mining, nuclear weapon production, nuclear explosions, fuel reprocessing, nuclear power plant accidents, nuclear fuel disposal, the usage of depleted uranium ammunition, etc. The large part of research into subsurface actinide transport refers to nuclear fuel disposal, i.e. to the long-term performance safety assessment for the “safety case” of nuclear fuel repositories.

It is obvious that the access of groundwater is crucial for all conceivable scenarios of actinide release from nuclear waste repositories. It should be differentiated between actinide chemistry in the near-field and actinide chemistry in the far-field of a nuclear waste repository. The most important chemical parameters governing actinide behavior are redox state, pH value, carbonate concentration, ionic strength, concentration of further complexants (sulfate, chloride, phosphate, fluoride, organics) and temperature. Because actinide ions in the same oxidation state have similar core structures, such species have similar chemical properties. In oxidized waters the actinides tend to occur in the hexavalent state (U, to some degree Pu) or the pentavalent state (Np, to some degree Pu). In these states they have a relatively high solubility and form readily soluble and stable complexes with the carbonate normally available in groundwaters or in the near-field solutions. This makes them waterborne and resistant to adsorption onto mineral surfaces, i.e. actinides can be very mobile in oxidized waters. In reduced waters the actinides typically possess their lower oxidation states, i.e. they are tetravalent (U, Np, Pu) or trivalent (Am, Cm, to some degree Pu). In these oxidation states they are prone to hydrolysis; they

are sparingly soluble (form solid phases) and tend to adsorb onto rock surfaces. More detailed information about actinide chemistry in environmental waters can be found in reviews by Silva and Nitsche (1995) or by Choppin (2003).

Fig. 1 shows the valence states of several critical radionuclides including actinides in a typical groundwater (Hu et al., 2008). The figure reflects that uranium needs strongly reducing conditions to occur in the tetravalent state whereas plutonium can be tetravalent even in only mildly reducing waters. Neptunium lies in between. Thorium is always tetravalent. Even though the surface waters encountered by humans in the biosphere are normally oxidic, the majority of the waters in the earth's crust and in particular the waters of the deeper zones are typically anoxic and reducing. Therefore, also the conditions in nuclear waste repositories (e.g. Delecaut et al., 2002, 2004), flooded uranium mines (e.g. Suutarinen et al., 1991) or deep groundwater horizons (e.g. Kalmykov et al., 2011) in their undisturbed states are reducing, which should support the tetravalent oxidation state of U, Np and Pu. Moreover, it has been shown that Pu is often tetravalent even under aerobic conditions (Bondietti et al., 1976; Champ et al., 1982; Conradson et al., 2011; Efurud et al., 1998; Ewing et al., 2010; Hu et al., 2008; Kalmykov et al., 2007; Menard et al., 1998; Pirlet, 2001; Romanchuk et al., 2011; Santschi et al., 2002). Pu(V) can be reduced under aerobic conditions at the surface of redox-reactive minerals such as ferrous oxides, and this reduction seems even possible at the surface of non-redox-reactive minerals like quartz, gibbsite, clay or hematite (Kersting, 2013; Maher et al., 2013; Romanchuk et al., 2011; Walther and Denecke, 2013; Zavarin et al., 2012). The mechanism of the latter reaction is not yet fully understood. Hu et al. (2008) reported that also Np(V) can be reduced to Np(IV) under aerobic conditions.

Actinides in their lower valence states tend to be immobile in the environment. However, as mentioned, tetravalent actinides may become waterborne if they are transformed into a colloidal form which makes the investigation of colloid-borne forms of An(IV) an issue. In the case of colloid-facilitated transport of contaminants the classical two-phase transport

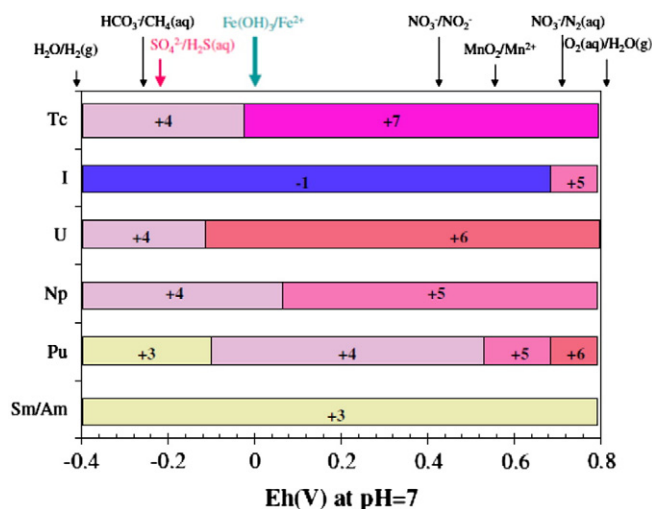


Fig. 1. Expected dominant oxidation states of several radioelements as a function of standard redox potential under pH 7 in a natural groundwater from the Nevada Test Site. Water at equilibrium with atmospheric CO_2 . Arrows at the top of the figure show the expected redox potentials for common redox couples in the groundwater. According to Hu et al. (2008). With permission.

concept must be abandoned and a third phase (the mobile nanoparticles) needs to be taken into consideration (see e.g. McCarthy and Zachara, 1989). Purely thermodynamic approaches will fail for colloid-facilitated transport (Kim, 2000, 2006).

2.2. Types of An(IV) colloids

A variety of colloid types can potentially play a role in subsurface radionuclide transport. Often these colloid types are divided into “intrinsic colloids” and “pseudocolloids” (cf. Kim, 1994; Silva and Nitsche, 1995). The former consist of polymerized complexes of the heavy metal cations formed by condensation of hydrolyzed metal ions with the metal cations linked by anions (cf. Geckeis et al., 2011). Actinide(IV) ions are bound by inclusion into the structure of the intrinsic colloids which can result in a relatively high chemical stability of the An(IV) colloids of this type (Geckeis, 2004). Pseudocolloids, on the other hand, are formed by the adsorption of radionuclides onto pre-existing natural colloids of the groundwater such as clay mineral, iron oxyhydroxide, alumina or humic colloids (groundwaters typically contain about 10^8 to 10^{14} particles L^{-1} of pre-existing colloids which can act as “carrier colloids” for contaminants; cf. Degueldre et al., 1989, 1996, 2000; Kim et al., 2005; Swanton, 1995). Because of their differences in structure, actinide intrinsic colloids and actinide pseudocolloids have also been named “homogeneous” and “heterogeneous” actinide colloids (Kurosawa et al., 2006a; Möri et al., 2003). As far as hypothetical leakage of nuclear waste repositories is concerned, intrinsic An(IV) colloids are primarily predicted for the near-field of the repository (Geckeis et al., 2011; Maher et al., 2013) whereas pseudocolloids are anticipated for both the near-field and the far-field (Smith and Degueldre, 1993).

2.3. Preconditions for colloid-facilitated An(IV) transport

The following conditions must be fulfilled to generate mobilizing effects of colloids on radionuclide subsurface transport (Beard, 2013; Ryan and Elimelech, 1996; Smith and Degueldre, 1993):

- (i) Colloids must be present in a non-negligible concentration,
- (ii) The colloids must be mobile and in stable suspension,
- (iii) There must be stable binding between the colloids and the radionuclides (slow reversibility or irreversibility).

If one of these conditions is not fulfilled, the role of colloids is negligible (cf. Fig. 2). If they all are met, colloids can significantly influence radionuclide transport. Model estimations for the proposed high-level nuclear waste geologic repository at Yucca Mountain, for instance, imply that colloid-facilitated transport of americium and plutonium leads to a 60-fold increase in the total effective dose equivalent for the relevant population after a delay time of >10 000 years (Contardi et al., 2001).

Among the three conditions, condition (iii), i.e. the question of the nanoparticles' chemical persistency, is of special importance (Bouby et al., 2011; Geckeis and Rabung, 2008; Grolimund et al., 1996; Huber et al., 2011; Kurosawa et al., 2006a; Ryan and Elimelech, 1996; Vilks and Baik, 2001). As particles that are not persistent are carried beyond a region in which the dissolved and colloid-borne contaminants are in

equilibrium, the particles will release their contaminants (or will completely dissolve) and equilibrium between the mobile phases and the stationary rock or sediment phases will reestablish. Tetravalent actinides that become released from the colloids in such a situation will readily adsorb onto the stationary phases and actinide transport will cease. However, as the strength of the contaminant-colloid association increases, the time to reach equilibrium increases, resulting in increased distances for colloid-facilitated transport (Ryan and Elimelech, 1996).

Condition (ii), too, is of high relevance. It is obvious that only suspended An(IV) nanoparticles that do not aggregate and sediment or adsorb onto host rock surfaces will be mobile. The nanoparticle–water interaction (hydrophilicity vs. hydrophobicity; cf. Silva and Nitsche, 1995) and the type of colloid-chemical stabilization (DLVO¹ behavior vs. non-DLVO behavior; cf. Hennig et al., 2013 and references therein) are crucial for condition (ii). The influence of ionic strength on colloid mobility may serve as an example of a field of active research. For several nuclear waste repository concepts such as those in rock salt (Germany) or in Opalinus Clay (Switzerland), the water potentially in contact with the waste after fuel container failure has a high or even a very high ionic strength. This will strongly reduce the stability of colloids and will prevent nanoparticles from becoming mobilized. However, relatively fast transitions in water chemistry must be taken into consideration since glacial melt water intrusions during the aftermath of a possible future ice age or other perturbations by waters poor in electrolytes might decrease the ionic strength and mobilize deposited nanoparticles (Hölttä et al., 2013; Liu and Neretnieks, 2006). The understanding of such processes must be improved.

Even if tetravalent actinides are in a colloidal and waterborne form, they need not be mobile. Migration can be prevented if there is no way for movement for geometric and/or electrostatic reasons. In other words, filtration can prevent mobility. Thus, it is expected that only particles of <<10 nm are able to move through diffusion controlled Opalinus Clay (Joseph et al., 2013; Voegelin and Kretzschmar, 2002). For Boom Clay, the host rock of the projected Belgian nuclear waste repository, this limit seems to be at around 100 kDa (Maes et al., 2006). When researchers became aware that colloid-facilitated transport of radionuclides is conceivable, they suggested (cf. Bates et al., 1992) to protect the surroundings of nuclear waste repositories in crystalline rock from the entrance of radiocolloids by the aid of a geo-engineered barrier consisting of compacted bentonite. A question still under discussion is how dense the bentonite really must be to reliably hinder radiocolloid release. According to experiments with gold nanoparticles by Kurosawa et al. (1997, 2001), a saturated bentonite density of 1640 kg/m³ is sufficient to retain colloidal particles of ≥15 nm. Densities of 1800 kg/m³ can also filter significantly smaller nanoparticles (Kurosawa et al., 2006b). However, Wold and Eriksen (2003, 2007) found that relatively small macromolecules such as lignosulfate molecules (molecular weight: 30 kDa) or the molecules of the commercial soil humic standard from the International Humic Substances Society (IHSS) are able to pass through compacted bentonite by diffusion with very little physical hindrance which is independent of bentonite density. The argument that gold colloids are

¹ Theory developed by Derjaguin, Landau, Verwey and Overbeck (cf. Eastman, 2005).

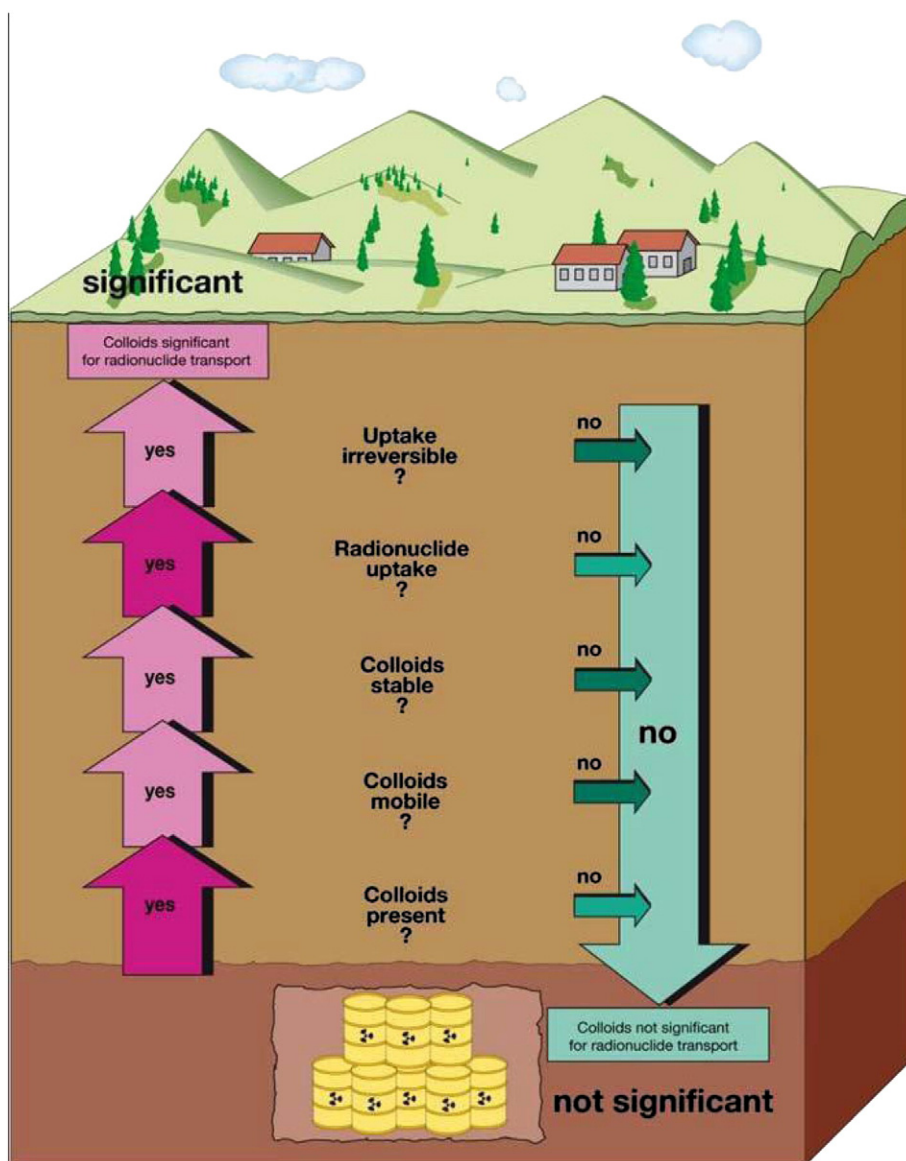


Fig. 2. Logical scheme illustrating that if one condition of colloid-facilitated transport is missing, colloids can be shown to be a minimal risk factor to the nuclear waste repository performance assessment. According to Beard (2013). With permission.

filtered by the compacted bentonite cannot be generalized to be valid for all types of colloids according to Wold and Eriksen.

Binding stability of the actinides in/on the colloids, colloid suspension stability, attachment probability and colloid filtration are also main issues in modeling colloid-facilitated transport of actinides. Several models of colloid-facilitated radionuclide transport do already exist (Buck and Wittman, 2009; Contardi et al., 2001; Flügge et al., 2010; Lührmann et al., 1998; Meier et al., 2003; NAGRA 94-06, 1994; Smith and Degueudre, 1993; Swanton, 1995). However, this research field is still developing. Further data from both well-defined laboratory experiments and field studies are needed (cf. BELBar D1.2, 2012). Direct observation of colloid transport processes by visualization via techniques such as tomography (Denecke et al., 2011; Enzmann and Kersten, 2006; Holzer et al., 2010; Huber et al., 2012; Kulenkampff et al., 2008) will also support modeling.

3. Actinide(IV) colloids in laboratory experiments

3.1. Colloids containing structural tetravalent actinides

3.1.1. An(IV) oxyhydroxide colloids

Under natural conditions, the solubility of tetravalent actinides is controlled by amorphous oxyhydroxides, $\text{AnO}_n(\text{OH})_{(4-2n)} \cdot x\text{H}_2\text{O}(\text{am})$, often also called hydroxides, $\text{An}(\text{OH})_4(\text{am})$, hydrous oxides, $\text{AnO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ or $\text{AnO}_2(\text{am}, \text{hydr})$ (cf. Altmaier et al., 2005; Neck and Kim, 2001).² In An(IV) solubility experiments concentration values

² A closer look into the structure of these “amorphous” oxyhydroxides (by high-resolution transmission electron microscopy) reveals that they are X-ray amorphous, but possess nanocrystallinity of the Fm3m lattice type (see e.g. Dzimitrowicz et al., 1984; Powell et al., 2011; Rousseau et al., 2009).

of the dissolved tetravalent actinides, $[\text{An}(\text{OH})_4(\text{aq})]$, which comply with the hydrolysis constants of the relevant An(IV) species and with the solubility product of the corresponding amorphous actinide(IV) oxyhydroxides could only be obtained if actinide colloids had thoroughly been removed from solution. If colloid removal (ultrafiltration, ultracentrifugation) was omitted, total actinide concentrations, $[\text{An}(\text{IV})]_{\text{tot}}$, that exceeded the true solubility, $[\text{An}(\text{OH})_4(\text{aq})]$, by a factor of about 100 were found due to the presence of An(IV) colloids (Altmaier et al., 2004, 2013; Bitea et al., 2003; Kim, 2006; Neck et al., 2002). Interestingly, the colloids of amorphous An(IV) oxyhydroxide responsible for these increased An(IV) concentrations, which are formed via the build-up of An(IV) oligomers and polymers (Knöpe and Soderholm, 2013; Knöpe et al., 2011; Soderholm et al., 2008; Walther et al., 2008, 2009; Wilson et al., 2011), seemed to be in equilibrium with the truly dissolved species of the respective tetravalent actinide; dilution of the colloidal suspensions below the thermodynamic solubility resulted in dissolution of the particles (Altmaier et al., 2004; Bitea et al., 2003; Walther and Denecke, 2013). These particles were hydrophilic and their colloidal stability was neither influenced by the ionic strength of the solution nor by the pH (within the pH range in which they do not re-dissolve by chemical dissolution). Thus these nanoparticles may be considered as large aqueous species that are in principle not different from ionic aqueous species. They showed sizes of a few nanometers to a few hundred nanometers and could be stable in the waterborne state over more than a year. Fig. 3 shows the concentration increase of waterborne Th(IV) due to the presence of Th(IV) oxyhydroxide colloids. Altmaier et al. (2004) determined equilibrium colloid saturation concentrations of $\log[\text{Th}(\text{IV})]_{\text{coll}} = -6.3 \pm 0.5$ and $\log[\text{Pu}(\text{IV})]_{\text{coll}} = -7.9 \pm 1.0$. Such colloids should be able to transform the “immobile” tetravalent actinides into a more mobile form than predicted from the solubility data of Th(IV) or Pu(IV) oxyhydroxide alone. They should be taken into account in nuclear waste repository performance assessment. It was surmised that An(IV) oxyhydroxide colloids do not play a role in the far-field of a nuclear waste repository, but that in the near-field they do (Geckeis, 2004).

The ability of the tetravalent actinides to form polymers and colloids in aqueous solution is not a new knowledge (cf. Costanzo et al., 1973; Ichikawa and Sato, 1984; Kim, 1986; Kraus and Nelson, 1950; Lloyd and Haire, 1978; Ockenden and Welch, 1956; Rai and Swanson, 1981; Schimmelpfennig, 2011; Silver, 2001; Triay et al., 1991). The structure of such polymers and colloids (typical intrinsic colloids) has been studied by the aid of spectroscopic techniques such as UV–Vis spectroscopy (Kim, 1986, 1991; Kraus and Nelson, 1950; Neck et al., 2001, 2007; Ockenden and Welch, 1956; Walther et al., 2007, 2009), extended X-ray absorption fine structure (EXAFS) spectroscopy (Dreissig et al., 2011; Ekberg et al., 2013; Hennig et al., 2013; Opel et al., 2007; Rothe et al., 2004, 2009; Schmidt et al., 2012; Soderholm et al., 2008; Walther et al., 2009; Wilson et al., 2011), X-ray scattering (Hennig et al., 2013; Thiyagarajan et al., 1990), electrospray ionization (ESI) mass-spectrometry (Rothe et al., 2009; Walther, 2011; Walther et al., 2008, 2009), etc.

There are indications that actinide(IV) oxyhydroxide colloids such as Pu(IV) oxyhydroxide colloids (Kersting, 2013) and U(IV) oxyhydroxide colloids (Kalmykov et al., 2011) also played a role in real-world scenarios (see also Section 4). However, Kersting (2013) assumed that Pu(IV) oxyhydroxide colloids tend to re-dissolve if they are transported into plutonium-free subsurface zones which corresponds to the above-mentioned findings for laboratory experiments that such particles dissolve on dilution to concentrations below the thermodynamic solubility. Therefore, Kersting, too, suggested that Pu(IV) intrinsic colloids should not be important in the far-field of a nuclear waste repository. Nevertheless, there are also findings according to which re-dissolution of Pu(IV) oxyhydroxide colloids in fresh water can be hindered due to aging of the nanoparticles during long spans of time and/or under the influence of increased temperature resulting in a conversion from hydroxide-bridged to oxygen-bridged polymeric Pu(IV) species (Choppin, 1983; Choppin and Jensen, 2010; Clark et al., 2010; Costanzo et al., 1973; Maher et al., 2013; Thiyagarajan et al., 1990) and stabilization of the colloid-borne state of the plutonium. Kalmykov et al. (2011) postulated that uranium had migrated as intrinsic U(IV)

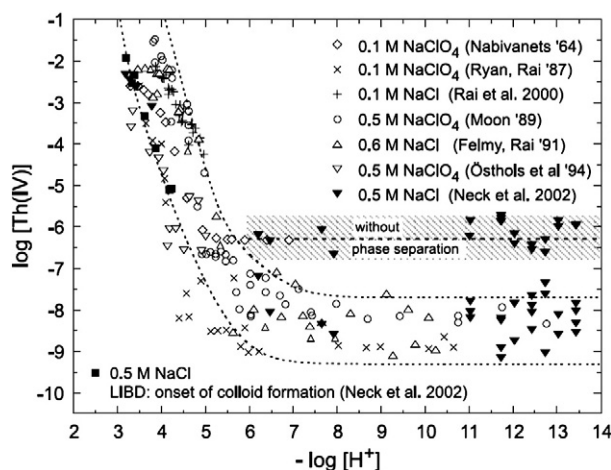


Fig. 3. Solubility of amorphous Th(IV) hydroxide or hydrous oxide at $I = 0.1$ – 0.6 M and 17 – 25 °C. The dashed curves represent lower and upper limits calculated with the solubility product and hydrolysis constants discussed in Neck and Kim (2001). The filled triangles in the hatched area show thorium concentrations measured without removal of colloids. According to Altmaier et al. (2004). With permission.

oxyhydroxide colloids over longer distances in an anaerobic aquifer at the Tomsk site, Russia. Leaching experiments on high-level (HLW) glass under reducing conditions, too, pointed to the formation of intrinsic An(IV) oxyhydroxide colloids (Inagaki et al., 1998). Intrinsic Pu(IV) oxyhydroxide colloids may also have played a part in the “colloid and radionuclide retardation experiments” at the Grimsel Test Site, Switzerland (Huber et al., 2011; Möri et al., 2003).

3.1.2. An(IV)-silica colloids

Dissolved silicic acid is ubiquitous in natural waters (Dietzel, 2000; Siever, 1972). It has long been known that there is affinity between tetravalent actinides and silica or silicic acid (cf. Amme et al., 2005; Costin et al., 2011, 2012; Deditius et al., 2012; Pointeau et al., 2009; Szenknect et al., 2013). Occasionally, there have been assumptions that actinides can form “metallo-silica” colloids in near-neutral waters such as waters able to enter nuclear waste repositories (Kim, 1994; Kunze et al., 2008; Ramsay, 1988; Ramsay et al., 1988). It was supposed that such silica-containing colloids might sometimes be difficult to detect (Kunze et al., 2008). Lieser and Hill (1992) and Peretroukhine et al. (2002) provided first positive evidence for the generation of silica-containing Th(IV) colloids using ultrafiltration. In Dreissig et al. (2011), Hennig et al. (2013) and Husar et al. (2012) more systematic studies on the nature of actinide(IV)-silica colloids are reported. An(IV)-silica colloids can be formed by co-precipitation in near-neutral solutions; concentrations of colloid-borne U(IV) and Th(IV) of up to 10^{-3} M were observed. These are An(IV) concentrations significantly higher than the concentrations of truly dissolved or colloiddally suspended waterborne tetravalent actinide species normally expected for the near-neutral pH range (see Fig. 3). The tendency to form such colloids is similar for the different tetravalent actinides (Zänker et al., 2012). The existence of this type of nanoparticles was proved by a series of methods such as photon correlation spectroscopy, ultracentrifugation and ultrafiltration. A particle size of <20 nm was found. The particles remained in the waterborne state over years; they showed increasing stability with increasing pH and increasing Si/An(IV) ratio. The internal structure of the particles was characterized by An–O–Si bonds that more and more replace the An–O–O bonds of the actinide oxyhydroxide structure with increasing silica concentration as was shown by EXAFS spectroscopy and other spectroscopic methods (Fig. 4). At the surface, the silica groups of the structure appear as silanol groups and, thus, contribute to the negative charge of the colloids (Hennig et al., 2013). It was concluded that the mechanism of colloidal stabilization of these particles has some similarity to colloidal “sequestration” of dissolved heavy metals by silicic acid, a phenomenon well known from trivalent heavy metals of high ion potential such as iron(III) (Browman et al., 1989; Doelsch et al., 2003; Dyer et al., 2010; Robinson et al., 1992) or curium(III) (Panak et al., 2005).

Following the above-cited definition that intrinsic colloids are formed by condensation of hydrolyzed metal ions and consist of these cations linked by anions, we would classify the An(IV)-silica colloids as intrinsic colloids. However, since the silica/An(IV) ratio within such colloids can be relatively high, these colloids also possess properties of pseudocolloids. The reasons for the striking stability of the silica-containing actinide(IV) colloids are not yet fully understood. Both DLVO forces (Eastman, 2005) and non-DLVO forces (Grasso et al.,

2002; Kobayashi et al., 2005; Yotsumoto and Yoon, 1993a,b) prevent these nanoparticles from coagulation, i.e. are responsible for their stability (cf. Zänker et al., 2013).

Geochemical scenarios that have the potential to cause the formation of waterborne An(IV)-silica colloids such as the mixing of waters containing U(VI), Np(V), etc. with reducing waters rich in silicic acid or the biogenic reduction of actinides in waters rich in silicic acid should be analyzed. The ability of tetravalent actinides to form mobile colloids with dissolved silicic acid even in very low Si concentration should be taken into account when considering geotechnical solutions for nuclear waste repositories such as the injection of grout silica sol into the bentonite/bedrock interface in order to seal the smallest hydraulic fractures of the bedrock (cf. Holmboe et al., 2011; Hölttä et al., 2009).

3.1.3. An(IV)-hydroxy aluminosilicate colloids

In several papers Kim et al. (2003a,b, 2005, 2007) and Panak et al. (2003) demonstrated the formation of another type of actinide colloids containing silica: actinide(III) hydroxy aluminosilicate colloids. Considering the above-mentioned similarity between the reaction of tetravalent and trivalent heavy metals with silicic acid, we assume that tetravalent actinides, too, are able to form actinide hydroxy aluminosilicate colloids, even though the existence of such colloids, to the best of our knowledge, has never been reported so far.

Two types of actinide(III) hydroxy aluminosilicate colloids have been found: particles that were stable at around pH 5 and particles that existed primarily between pH 7 and 9.5 (Kim et al., 2005; Panak et al., 2003). At pH >7 the actinides studied (trivalent curium and americium) can hardly be desorbed from the colloids while most of the actinide present can easily be removed from the nanoparticles produced at pH 5 (Kim et al., 2005). The size of the particles was in the range of 10 to 50 nm

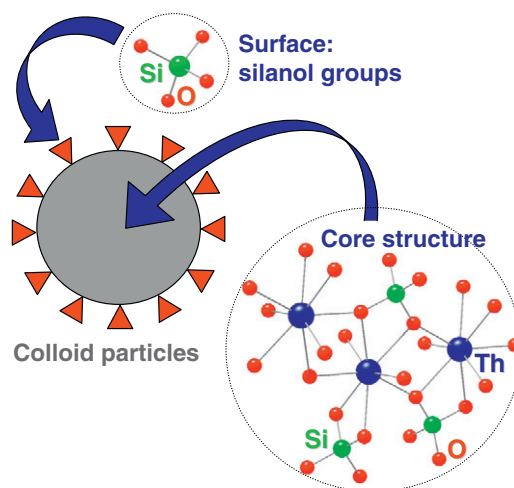


Fig. 4. Structure model for Th(IV)-silica colloids with the typical nearest neighbor environment. The near-order distances were determined with EXAFS (Th–O = 2.36–2.41 Å, N_O = 8.3–9.6, Th–Si = 3.23–3.26 Å, N_{Si} = 1.3–2.5) and HEXS (Th–Th distance of ~3.98 Å). It was not differentiated between oxo and hydroxo bonds in the drawing. The Th–O–Th bonds are increasingly replaced by Th–O–Si bonds with increasing silicic acid concentration at the moment of co-precipitation of Th and Si. This structure also results in the enrichment of silanol groups at the surface. Modified according to Hennig et al. (2013). With permission.

(Kim et al., 2003b). The particles were stable in the waterborne state over several months. From laser fluorescence spectroscopy experiments Kim et al. (2003b, 2005) and Panak et al. (2003) concluded that the trivalent actinides are incorporated into the structure of the hydroxy aluminosilicate particles, i.e. the trivalent actinides act as isomorphic substitutes for aluminum. Depending on whether the particles are formed from polysilicic acid or from monosilicic acid, the structure of these particles resembles imogolite or a mixture of sillimanite plus kaolinite (Kim et al., 2005). They are assumed to be precursors of clay mineral colloids (Geckeis, 2004; Geckeis et al., 2011; Panak et al., 2003). Also these particles might be regarded as intrinsic colloids if the above-mentioned definition that intrinsic colloids are formed by condensation of hydrolyzed heavy metal ions is followed. However, they may also be classified as pseudocolloids because their silica/An(III) and Al/An(III) ratios can be very high.

As mentioned, the existence of actinide(III) hydroxy aluminosilicate colloids strongly suggests that also tetravalent actinides are able to form hydroxy aluminosilicate colloids. The existence of such colloids should be tested.

3.1.4. An(IV) clusters formed by reaction with low molecular mass organic acids

Tetravalent actinides are able to form nanosized hexanuclear clusters with carboxylic acids or with amino acids whose size approaches or lies in the colloidal size range (Hennig et al., 2012; Knope and Soderholm, 2013; Knope et al., 2011; Takao et al., 2009, 2012). The organic acids act as bridging ligands in these clusters which prevent the formation of polynuclear hydrolysis species such as An(IV) hydrous oxide colloids. Not much is still known about the chemical stability, the colloidal stability and the mobility of the low molecular weight organic acid based An(IV) particles under environmental conditions.

3.2. Colloids carrying adsorbed tetravalent actinides

3.2.1. An(IV)-clay mineral colloids

Actinide(IV)-clay mineral colloids are a typical example of pseudocolloids. Bentonite colloids carrying An(IV) are probably the best-investigated sort of this colloid type. The particles may form at the near-field/far-field interface of nuclear waste repositories where smectite-like clay can be washed out from the compacted bentonite by groundwater due to the erosion of the geo-engineered bentonite barrier (Albarran et al., 2008; Geckeis, 2004; Geckeis et al., 2004; Huber et al., 2011; Missana et al., 1999, 2003, 2004; Norrfors et al., 2013). Whereas the ionic strength in the porewaters of bentonite is high enough to precipitate most of the colloids, the waters of the shear zone, where porewaters and groundwaters mix, can be poor in electrolytes and can support colloid stability. The bentonite colloids are stable in the waterborne state over months at sufficiently low ionic strength (see e.g. Missana et al., 2004). The behavior of An(IV)-bentonite colloids is controlled by the behavior of the bentonite component, the influence of the actinide on colloid stability can usually be neglected as was demonstrated for Th(IV)-bentonite colloids by Bouby et al. (2011). Therefore, the stability of pure bentonite colloids has extensively been studied (Albarran et al., 2008; Missana and Adell, 2000; Missana et al., 2003; Norrfors et al., 2013). These particles do not obey the DLVO theory. The binding of the tetravalent actinides onto the bentonite colloids is relatively

strong; desorption is kinetically inhibited; binding is possibly not fully reversible (Bouby et al., 2011; Geckeis and Rabung, 2008; Geckeis et al., 2004; Huber et al., 2011; Möri et al., 2003).

The transport of bentonite and other clay mineral colloids carrying tetravalent actinides such as tetravalent Th and tetravalent Pu through porous rock media has been investigated in both laboratory experiments (Abdel-Fattah et al., 2013; Albarran et al., 2008; Delos et al., 2008; Pratopo et al., 1993) and field experiments at the Grimsel Test Site, Switzerland (Geckeis et al., 2004; Huber et al., 2011; Kurosawa et al., 2006a; Möri et al., 2003). These experiments demonstrated the dramatic influence of bentonite colloids on actinide(IV) mobility.

Actinide(IV)-clay mineral colloids were also detected in solutions from nuclear waste glass corrosion experiments (Pu(IV)-smectite colloids; cf. 3.2.8), in groundwaters at the Nevada Test Site (clay and zeolite-like colloids carrying Pu(IV); cf. 4.2) and in aquatic suspensions of sediments from Lop Nor, China, to which Pu(IV) had been added (Xie et al., 2012).

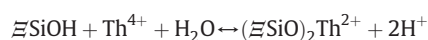
3.2.2. An(IV)-iron oxide colloids

Another type of pseudocolloids is iron oxide particles carrying tetravalent actinides. If water enters the near-field of a nuclear waste repository, waste container steel may corrode and iron-containing nanoparticles may form (Geckeis et al., 1998; Grambow et al., 1996; Kirsch et al., 2011; Seco et al., 2009). These particles are able to act as carrier colloids for radionuclides. If the processes are isolated from the access of air, the conditions are reducing and the actinides tend to be tetravalent. The iron of the corrosion products is mainly divalent, i.e. hydrous ferrous oxides together with some magnetite are typically formed (Grambow et al., 1996). The ferrous oxide nanoparticles are able to reduce actinides and to adsorb the resulting tetravalent actinides and can, thus, form An(IV) pseudocolloids. The behavior of such colloids has primarily been investigated under rock salt near-field conditions, i.e. at high ionic strengths. Under such conditions these pseudocolloids were very unstable and colloid-facilitated transport of An(IV) by this type of colloids is not expected to be relevant for nuclear waste repositories (Geckeis et al., 1998). Less is known about the behavior of iron(II) colloids at low ionic strength as in granitic groundwaters. Wang et al. (2013) reported the transport of U(IV) pseudocolloids under anoxic conditions in a wetland near an abandoned uranium mine. The carrier colloids were supposed to consist of $\text{Fe}(\text{OH})_2$ -organic matter assemblages. If the system is not isolated from air and the conditions are oxidic, only thorium and plutonium will usually occur in their tetravalent form (cf. 2). Iron is trivalent in this case and the candidate Fe carrier colloids consist of ferric oxides such as ferrihydrite, goethite, akaganeite, and hematite. Th(IV) and Pu(IV) are known to adsorb strongly onto such oxides (see e.g. Powell et al., 2011). Information on the transport behavior of the resulting An(IV) pseudocolloids is contradictory. Often it is assumed that the mobility of colloids consisting of ferric oxides is low because of their low colloidal stability (Vilks et al., 1998); ferric oxide colloids have even been shown to scavenge and immobilize dissolved actinides such as hexavalent uranium due to their low electrostatic stabilization (Brendler et al., 2002; Zänker et al., 2000, 2003). On the other hand, it was reported that at the Mayak site, Russia, mobile hydrous ferric oxide colloids transported tetravalent plutonium in groundwater over more than 4 km

within 55 years (cf. 4.3). The mechanisms of iron(III) oxide colloid transport are obviously not yet fully understood; the stabilization of these particles by dissolved organic matter seems to be crucial.

3.2.3. An(IV) colloids generated by sorption onto silica particles

Silica particles, too, can act as carriers and form An(IV) pseudocolloids. James and Healy (1972) studied the adsorption of Th(IV) onto synthetic quartz particles by measuring the electrophoretic mobility of the particles. They explained the attachment of thorium to the particles by surface precipitation due to the high electric field at the solid–liquid interface which was expected to lower the interfacial solubility product of the thorium hydroxide by several orders of magnitude. An alternative explanation was provided by Östhols (1995) who attributed the adsorption of Th(IV) onto commercial pyrogenic silica to surface complexation according to the equation



This was concluded from both batch experiments based on titrations on silica in the presence of thorium and modeling work. It is in accordance with the findings of EXAFS spectroscopy experiments carried out later which showed that the tetravalent thorium is bound to the silica by a monodentate bridging coordination (Östhols et al., 1997).

The latter explains the difference between the sorption of An(IV) onto pre-formed silica particles and the formation of the An(IV)–silica particles described in 3.1.2 which are produced by co-precipitation of An(IV) oxyhydroxide and silica. Östhols (1995) observed maximal thorium coverage of the pre-formed silica particles of 10^{-4} mol/g silica. This is equivalent to a molar Th/Si ratio of 6×10^{-3} . According to Östhols (1995), it seems therefore unlikely that pre-formed silica particles will act as efficient Th scavengers under environmental conditions since Fe and Mn oxides are much more likely to be the main sorbents. On the other hand, for the co-precipitated An(IV)–silica colloids containing structural An(IV) (3.1.2) molar An(IV)/Si ratios of around 1 are typically observed which may make them much more important scavengers of An(IV).

Another mechanism of Pu(IV) attachment to pre-formed silica particles was described by Batuk et al. (2012). These authors found that PuO₂ nanoparticles were deposited from Pu(V) solutions on amorphous silica, presumably by the relatively unspecific Pu reduction reaction observed for a number of mineral surfaces (cf. 2.1).

3.2.4. An(IV)–humic colloids

There is a considerable amount of literature dealing with the reactions of humic and fulvic acid with actinides (including tetravalent actinides). It would be beyond the scope of this review to give a comprehensive overview of this literature. Although there are discussions that humic and fulvic acids might be species of intrinsically only low molecular weight (several hundreds of Da) that form aggregates held together by hydrogen bonding, non-polar interactions and polycation interaction (cf. Bryan et al., 2012; Leenheer and Croue, 2003 and literature therein), there is agreement that humic and fulvic substances also possess pronounced macromolecular characteristics. Nowadays, macromolecular chemistry is not

automatically seen as colloid chemistry and macromolecules are not automatically seen as colloids (Cosgrove, 2005). However, the observed sizes of humic and fulvic acid macromolecules lie in the lower nanometer range (Mertig et al., 1999; Schimpf and Petteys, 1997), i.e. they fall into the size range of colloids; humic and fulvic acid molecules, thus, should be regarded as colloids. Consequently, also the complexes that are formed by humic and fulvic acid with tetravalent actinides should be taken as colloids.

Tetravalent thorium (Cacheris and Choppin, 1987; Choppin and Cacheris, 1990; Choppin and Nash, 1981; Denecke et al., 1999; Geckeis et al., 2002; Reiller, 2005; Reiller et al., 2003, 2008; Schild and Marquardt, 2000), tetravalent uranium (Delecaut et al., 2004; Li et al., 1980; Reiller et al., 2008), tetravalent neptunium (Artinger et al., 2000; Pirlet and Van Iseghem, 2003; Schmeide et al., 2005; Zeh et al., 1999) and tetravalent plutonium (Bondietti et al., 1976) have been reported to form such complexes with the humic polyelectrolytes. Whereas tetravalent actinides are very prone to hydrolysis and precipitation in humic-free near-neutral solutions, they can become stabilized in the water-borne state by the formation of humic complexes which increases their mobility. In a first step, the actinides are bound to the carboxylic and possibly phenolic groups of the humics as inner-sphere complexes (Denecke et al., 1999; Schild and Marquardt, 2000; Schmeide et al., 2005), a reaction which is largely reversible. Desorption experiments with a competing complexant or a chelating resin (Chelex 100) showed that this reversibility is reduced or even partly eliminated with increasing contact time between the tetravalent actinides and the humics before the desorption test (Artinger et al., 2003; Bouby et al., 2002; Cacheris and Choppin, 1987; Choppin and Cacheris, 1990; Geckeis et al., 2002; Schild and Marquardt, 2000). Humic substances bind metal ions in two modes – there is a mode of an exchangeable fraction and there is a mode of slow transfer from the exchangeable fraction into a non-exchangeable fraction (cf. Bryan et al., 2007). Several explanations for this phenomenon have been suggested. The kinetic hindrance of An(IV) dissociation after a certain span of contact time has been attributed to a slow transfer of the actinide ions into the interior of the humic molecules (Cacheris and Choppin, 1987; Choppin and Cacheris, 1990; Engebretson and von Wandruszka, 1998). Geckeis et al. (2002) suggested that bridging of several humic molecules by the polyvalent actinides and the formation of small associates (“wrapping” of the actinides) should be the reason for the strong binding. In a similar way, Lippold et al. (2012) assumed that the actinide does not move within the humic molecule but the local organic structure around the actinide changes slowly. It is also very important that the non-exchangeable heavy metal fraction includes particles consisting of polymerized metal species plus humic–humic associates (Artinger et al., 2003; Kim, 2006; Kim et al., 1999). This is discussed in 3.2.5.

3.2.5. Humic substance stabilized inorganic colloids containing An(IV)

As discussed in more detail in Section 2.3, both the reversibility of actinide binding onto/into the colloids and the rate of dissociation of the actinides from the colloids are critical for the question of whether or not colloid influences on actinide transport in the environment exist. Therefore, a second line of approach for elucidating the role of humic and fulvic acid for

An(IV) transport had been adopted. The behavior of naturally-occurring tetravalent thorium and uranium and their analogs Zr(IV), Hf(IV) and Ti(IV) in samples of humic-rich waters such as groundwaters from the Broubster site, UK, or the Gorleben site, Germany, was investigated (Artinger et al., 2003; Bouby et al., 2002; Geckeis et al., 2002; Read and Hooker, 1989). It was shown that there is a direct correlation between the concentrations of the tetravalent trace metal ions and the dissolved organic carbon in such waters, indicating that the waterborne state of tetravalent metals is attributable to the presence of humics. Desorption experiments similar to those discussed in 3.2.4 were carried out. They revealed that the natural thorium inventory and the thorium added in the laboratory show comparable dissociation kinetics. However, the rate constant of dissociation of the naturally-occurring Th from the humics was much lower than that of the added Th (Artinger et al., 2003). Obviously, the long-term interaction of thorium and the humics in nature leads to a chemical association state different from that of laboratory-added thorium (Bouby et al., 2002); there are even indications that some of the natural thorium is bound irreversibly to the humics (Geckeis et al., 2002). Field-flow fractionation (FFF) experiments revealed that the strongly-bound natural thorium does not form simple humate or fulvate complexes as those discussed in 3.2.4. The natural thorium is incorporated in inorganic “composites” which consist of various metal compounds such as Al(III), Cr(III), Fe(III), REE(III), Zr(IV), and U(IV) compounds and which are peptised by humic or fulvic acid (Bouby et al., 2002; Geckeis et al., 2002). In the case of purified Gorleben humic acid, FFF showed that these objects had a size of up to 35 nm. The existence of a population of relatively large nanoparticles (70 to 160 nm) in natural humic acid was also demonstrated for solutions of purified Aldrich humic acid using photon correlation spectroscopy (Zänker et al., 1999) and atomic force microscopy (Mertig et al., 1999). Such relatively large nanoparticles are an inherent constituent of natural humic acid. They are very inert and do not disintegrate on diluting the humic acid solution or on changing its pH. Even acid treatment does not completely destroy these particles (Geckeis et al., 2002). On the other hand, these nanoparticles prove to be relatively stable colloids; they are stabilized in the water-borne state due to the adsorption (and possibly also incorporation) of humic or fulvic acid. The ability of humic substances to stabilize inorganic natural colloids and other nanoparticles in the waterborne form, e.g. by increasing their electrostatic repulsion, has long been known (e.g. Liang and Morgan, 1990; Schierz and Zänker, 2009; Tipping and Higgins, 1982; Wilkinson et al., 1997).

3.2.6. Further An(IV)-NOM colloids

Natural organic matter (NOM) such as extracellular polymeric substances (Merroun and Selenska-Pobell, 2008; Neu et al., 2010), polysaccharides (Quigley et al., 2002; Wilkinson et al., 1997) and cutin-like substances (Xu et al., 2008), too, consist of organic macromolecules which are able to form nano-sized colloids in natural waters that carry tetravalent actinides. Also lignin particles have been discussed as potential carriers of heavy metals (Krachler et al., 2012).

3.2.7. An(IV) biocolloids

Microorganisms can influence actinides in various ways; a comprehensive overview of these influences would be beyond

the scope of this article. There is a considerable number of bacteria having the ability to reduce actinides to the tetravalent state (Behrends et al., 2012; Sharp et al., 2011; Wall and Krumholz, 2006). The reaction typically results in the production of An(IV) dioxide nanoparticles such as UO₂ particles which are attached onto the biomass, i.e. this enzymatic reduction tends to immobilize the actinides. However, there are still open questions:

- The immobility of the generated AnO₂ nanoparticles cannot be taken for granted as had already been pointed out by Suzuki et al. (2002).
- There have been findings which show that the reaction product need not be pure AnO₂ but can also contain other components such as structural phosphate (Bernier-Latmani et al., 2010) and possibly further anions. Little is known about the mobility of such particles.
- Microorganisms carrying An(IV) may be mobile and may act as An(IV) pseudocolloids. In deep groundwater from Olkiluoto (Finland), Pedersen et al. (2010) found a number of suspended microorganisms of $3.1 \cdot 10^6$ to $2.1 \cdot 10^8$ cells L⁻¹ (note, however, that in comparison to the typical numbers of abiotic nanoparticles in groundwaters given in Section 2, this is a relatively small particle number; it remains to be elucidated if the few planktonic bioparticles can significantly increase actinide(IV) mobility).
- Microorganisms produce siderophores which can mobilize tetravalent actinides by the formation of truly dissolved complexes (Johnsson et al., 2009).

The role of microbial processes and biocolloids for actinide behavior needs further research.

3.2.8. An(IV) colloids generated by waste form corrosion

A variety of colloid types were observed in laboratory experiments with waste forms corroding in water. Most of the experiments were performed on nuclear waste glass under oxidizing conditions (Ahn et al., 1993; Avogadro and de Marsily, 1983; Bates et al., 1992; Buck and Bates, 1999; Buck and Wittman, 2009; Buck et al., 1994; Ebert et al., 1994; Feng et al., 1994; Inagaki et al., 1998; Kim et al., 1985; Menard et al., 1998). They led to the formation of a remarkable number of new phases such as smectite, kaolinite, iron oxides, magnesium oxide, weberite, uranophane, boltwoodite, nagelschmidtite, calcite, dolomite and further ones. Many of these phases can be regarded as potential carrier colloids for tetravalent actinides and some of them really seem to act as such. Furthermore, the formation of intrinsic An(IV) colloids cannot be ruled out. Two mechanisms can result in the formation of secondary mineral colloids. On the one hand, secondary minerals can precipitate from solution and form colloids (“nucleation”). On the other hand, colloids can be released into the solution by spallation from an alteration layer on the waste glass which consists of siliceous gel and clay and is enriched in sparsely soluble heavy metals (Ahn et al., 1993; Avogadro and de Marsily, 1983; Bates et al., 1992; Buck and Bates, 1999; Buck et al., 1994; Feng et al., 1994; Menard et al., 1998; Pirlet, 2001). Fortunately, glass corrosion leads to high ionic strengths which makes colloids unstable and causes them to flocculate and to settle out from the solutions. However, if large amounts of groundwater poor in electrolytes contact the glass reaction site of a waste

repository, re-suspension of the colloids is supposed to be possible (Feng et al., 1994).

Only few experiments on waste glass under reducing conditions have been done. The release ratio of colloid-borne actinides to truly dissolved actinides is higher under reducing than under oxidizing conditions (Inagaki et al., 1998). Several aerobic leaching experiments have also been performed on spent fuel that was not vitrified (Buck et al., 2004; Finn et al., 1994; Kaminski et al., 2005). They resulted in the formation of secondary phases such as schoepite and soddyite which also have the potential to form colloids suited to act as carriers of actinides such as tetravalent plutonium (Buck et al., 2004).

It is needless to say that the processes resulting in colloid formation due to waste form corrosion are significantly more complex than those observed in well-defined experiments as the experiments described in Section 3.1. In the case of waste form corrosion it is difficult to identify all mechanisms behind colloid formation as it may be possible for the experiments described in Section 3.1. On the other hand, the results described in Section 3.1 can guide the interpretation of the more complex tests. For instance, the experiments on nuclear waste glass by Feng et al. (1994) resulted in the generation of very silica-rich colloids. Feng et al. emphasized that this richness in silica made these colloids similar to a system of pure silica colloids. It is obvious that the investigations discussed in 3.1.2 and 3.1.3 can contribute to the understanding of such colloids.

3.2.9. An(IV) colloids from cementitious systems

Cement is an important constituent of a nuclear fuel repository's near-field, be it as a construction material or as the vault backfill. Concrete undergoes significant alterations when it reacts with water. In particular, the formation of calcium silicate hydrates (CSH) is of importance for radionuclide behavior. It has been shown that CSH phases can incorporate significant amounts of trivalent and tetravalent actinides (Gaona et al., 2011; Stumpf et al., 2004; Tits et al., 2003). It has also been shown that cementitious systems release colloidal particles (Fujita et al., 2003; NAGRA 94-06, 1994; Ramsay et al., 1988; Swanton and Vines, 2003; Wieland and Spieler, 2001; Wieland et al., 2004). Such are CSH particles or CaCO_3 particles. Especially CSH colloids have the potential to carry tetravalent actinides. However, the degradation of concrete by water also results in a high pore water ionic strength which makes the colloids very unstable. According to Wieland and Spieler (2001) and Wieland et al., (2004), cementitious near-field colloids should, thus, exert only a minor effect on radionuclide migration. Research regarding scenarios which include the access and admixture of water poor in electrolytes is still needed.

4. Actinide(IV) colloids in real-world scenarios

4.1. General

For obvious reasons, there have not been real-world actinide release scenarios with nuclear waste repositories. However, human activities gave rise to a number of incidents resulting in the intentional or unintentional introduction of actinides into the environment (cf. IAEA-TECDOC-1663, 2011; Maher et al., 2013; Oughton and Kashparov, 2009; Salbu and Lind, 2011;

Walther and Denecke, 2013). These incidents typically caused site-specific radiation protection problems for the population involved; therefore, the behavior of the radionuclides after entering the environment has often been thoroughly investigated at such sites. However, actinide behavior at the involved sites can also provide general information on An(IV) colloid behavior in the environment which is useful for performance assessment of nuclear waste repositories. In the following, several selected examples referring to colloid-facilitated An(IV) transport are given. The identification of the actinide transport mechanisms is more difficult in real-world scenarios than in laboratory experiments and in many cases there are controversies whether or not the observed transport of an actinide really was due to the influence of colloids (see e.g. Cantrell and Riley, 2008).

4.2. An(IV) colloids from underground nuclear tests

A considerable number of underground nuclear weapon tests have been performed by countries such as USA, Soviet Union, France, UK, and China. The best-investigated test site regarding post-test radionuclide behavior is the Nevada Test Site, USA (Kersting and Zavarin, 2011; Kersting et al., 1999, 2003; Zhao et al., 2011). It was found there that a small but significant fraction of the plutonium produced during one of the nuclear tests, the Benham test in 1968, had migrated >1 km away from ground zero within about 3 decades which could only be explained by transport within the groundwater. Plutonium was expected to be tetravalent in the groundwater (Hu et al., 2008). Kersting and co-workers assumed that the Pu(IV) was transported due to attachment to colloids which were primarily clay and zeolite colloids with a prevailing size of 10 to 100 nm. There was no evidence that plutonium had migrated as intrinsic PuO_2 colloids. In the tunnel system of the Rainier Mesa area at the Nevada Test Site, where a total of 62 detonations had been conducted up to 1992, plutonium was found to be associated with dissolved organic matter (Zhao et al., 2011). The latter presumably resulted from tunnel lagging, wood debris, drilling fluids, and their microbial decomposition products. This organic matter was assumed to be similar to humic acid.

4.3. An(IV) colloids from facilities of fuel production and fuel reprocessing industries

Production of uranium-based fuel, spent fuel reprocessing, production of plutonium, etc. caused actinide releases to the environment at numerous sites. Often it was surmised or made evident that actinide colloids have played a role in actinide transport at these sites. We give three examples for such sites, all related to nuclear weapons production. Further examples can be found in the reviews by Kersting (2013), Maher et al. (2013), Walther and Denecke (2013) and references therein.

4.3.1. Mayak Site (Radiochemical Production Association "Mayak", South Urals), Russia

Significant amounts of NaNO_3 brines which contained huge concentrations of radionuclides including actinides were discharged into a pond without outlet called Lake Karachai at the Mayak Site. From there the solutions seeped into the groundwater. The plutonium migrated away there over a

distance of more than 4 km within 55 years. At that distance, >90% of the plutonium was associated with the colloidal fraction of the groundwater which was evidenced by ultrafiltration (Kalmykov et al., 2007, 2011; Novikov et al., 2006). The plutonium was tetravalent. It was attached to carrier colloids of hydrous ferric oxide (Kalmykov et al., 2007, 2011; Novikov et al., 2006) or of a mixture of chlorite and hydrous ferric oxide (Malkovsky et al., 2012), i.e. it was transported in the form of pseudocolloids. These colloids were obviously stabilized in the water-borne state due to coating with organic substances such as humic and fulvic acids and technology-related organics (Malkovsky et al., 2009, 2012).

4.3.2. Tomsk Site (Siberian Chemical Combine), Russia

Injection of low- and intermediate level liquid radioactive waste into freshwater horizons is a method of radioactive waste disposal applied at several sites in Russia (Rybalchenko et al., 2005; Shestakov et al., 2002; Zubkov et al., 2005). At the Tomsk Site uranium-containing aerobic waste solution is injected into reducing groundwater ($E_h = -118$ mV). Using ultrafiltration, Kalmykov et al. (2011) found the uranium in a colloid-borne form in the groundwater, indicating the reduction of U(VI) to U(IV). Based on the results of NanoSIMS measurements Kalmykov et al. explained the behavior of U by the formation of intrinsic U(IV) hydroxide colloids.

4.3.3. Rocky Flats Environmental Technology Site (RFETS), Colorado, USA

Nearly 40 years of plutonium production at the RFETS had led to significant Pu contamination of the site which was very heterogeneously distributed (Conradson et al., 2011; Santschi et al., 2002). Most of the Pu was in the top 12 cm of the soil (Conradson et al., 2011). According to ultrafiltration, the Pu occurred mainly in the particulate ($\geq 0.45 \mu\text{m}$) and the colloidal (3 kDa to $0.45 \mu\text{m}$) forms. Its oxidation state was IV. It was associated with organic material such as humic and fulvic acid (Santschi et al., 2002). There were no indications as to the existence of intrinsic PuO_2 colloids. Groundwater was not a major pathway for the plutonium. Migration occurred through sedimentation and re-suspension of small particles by wind and surface water.

4.4. An(IV) colloids from nuclear reactor accidents

Explosions and fire in the reactor core of unit 4 of the Chernobyl nuclear power plant on April 26, 1986 resulted in the dispersal of about 6 tons of irradiated fuel (Burns et al., 2012) as air-borne particles. Most of these “hot particles” had a size of $<10 \mu\text{m}$ (Boulyga and Becker, 2001, 2002; Kashparov et al., 1999, 2009; Salbu et al., 1994) and deposited within the 30-km exclusion zone around the power plant (Matsunaga et al., 2004). They contained, for instance, a total $^{239} + ^{240}\text{Pu}$ activity of $1.5 \cdot 10^{13}$ Bq (Kashparov et al., 2003). The isotopic composition of the individual hot particles provides information on their fuel burnup and their origin within the reactor core (Boulyga and Becker, 2001, 2002; Mietelski et al., 2002; Mironov et al., 2002, 2005, 2009). Most of these particles are larger than colloids (cf. Section 1); they possess only low mobility in the environment. In a soil column experiment by

Ivanov (2009), the highest mobility was found for the smallest particle size class (0 to $2 \mu\text{m}$). After the accident a substantial fraction of the uranium of the particles was tetravalent, in later years more and more uranium became hexavalent due to oxidation (Mironov et al., 2002; Mironov et al., 2005). The resistance of the particles to weathering depends on the local soil pH and on the degree of oxidation of the fuel. The latter also relates to the moment of release during the reactor accident sequence (explosion vs. fire). After the dissolution of the fuel particles, the actinides and fission products are transformed into new chemical forms such as soluble carbonate complexes, organic complexes or colloids. Plutonium which might be tetravalent even under aerobic conditions (cf. 2.1) showed a relatively high tendency to form complexes/colloids with natural organic matter (Levchuk et al., 2009, 2012; Matsunaga et al., 2004).

Much smaller amounts of actinides than in Chernobyl were released by the accident of the Fukushima Daiichi nuclear power plant, Japan, in 2011. Not much is still known about the chemical forms of these actinides in the environment (Burns et al., 2012; Fujiwara et al., 2012; Kirchner et al., 2012; Zheng et al., 2012), but the formation of “hot particles” and actinide colloids is highly probable.

5. Summary and outlook

Actinide(IV) colloids are increasingly in the focus of research into environmental radionuclide transport. We give a compilation of most of the An(IV) colloids described in the hitherto literature. An(IV) colloids may occur in a variety of environmental scenarios. Our special (but not exclusive) focus is on An(IV) colloids in the context of nuclear fuel repositories. Thermodynamic approaches exclusively based on solubility and sorption probability fail if An(IV) transport is colloid-facilitated. If tetravalent actinides become colloid-borne, they may migrate as fast as the water flow velocity (or, due to size/charge exclusion effects, even faster). This is most likely the reason why An(IV) transport distances of kilometers within few decades have sometimes been reported for real world scenarios for which traditional models predict transport distances of only centimeters or very few meters.

There is already a certain amount of knowledge as to the formation of An(IV) oxyhydroxide, An(IV)-silica, An(IV)-clay mineral (in particular An(IV)-bentonite) and An(IV)-humic colloids. Less is known about the formation and nature of iron oxide-related, waste-form related, cement-related and biological colloids of tetravalent actinides. The existence of An(IV)-hydroxy aluminosilicate colloids (3.1.3) has not even been proved so far; we only hypothesize it (though the existence of such colloids is highly probable because of the now well-known affinity of silicic acid for both tetravalent actinides and aluminum). Even the existence of actinide(IV)-silica colloids has only recently been demonstrated in laboratory studies (Dreissig et al., 2011; Hennig et al., 2013) which is remarkable since silicic acid is ubiquitous in nature and An(IV)-silica colloids form quite readily in laboratory experiments. The formation of An(IV)-silica colloids should normally be even more probable in near-neutral groundwaters than the formation of An(IV) oxyhydroxide colloids because the probability to react with a silica species is higher for an An(IV) hydroxo complex than the probability to react with another

An(IV) hydroxo species.³ Similarly, also the formation of An(IV)-hydroxy aluminosilicate colloids should be more likely than the formation of An(IV) oxyhydroxide colloids since free aluminum ions, too, are normally present in environmental waters at concentrations significantly higher than actinide concentrations. The existence of actinide(IV) oxyhydroxide, actinide(IV)-silica and actinide(IV)-hydroxy aluminosilicate colloids in nature should be tested by searching them in natural waters (as e.g. in reducing waters from the vicinity of undisturbed uranium ore deposits). Table 1 gives a brief overview of the colloid types discussed in this article and the hitherto existing evidence of their occurrence in laboratory experiments, field experiments and real environmental scenarios.

The properties of An(IV) colloids most important for their migration in environmental waters are

- (i) Particle size,
- (ii) Colloid-chemical stability (resistance to aggregation and adsorption onto the stationary phase) and
- (iii) Chemical stability (resistance to disintegration).

Particle size and colloid-chemical stability govern the behavior of An(IV) colloids in particular in the near-field of nuclear waste repositories. Therefore, a geo-technical barrier of compacted bentonite is an effective means to prevent the release of An(IV) colloids by filtering them out. The high ionic strength typically prevailing in the near-field of a nuclear waste repository, too, creates a tendency to prevent migration of colloids since it results in their aggregation, sedimentation and adsorption on the stationary phase. However, there are still open questions. Macromolecules of 30 kDa (lignosulfate) were observed to diffuse through the pores of bentonite, independently of the bentonite density (Wold and Eriksen, 2003). Humic substances, too, proved to be able to diffuse through compacted bentonite (Wold and Eriksen, 2007). This raises the question if An(IV) humate complexes (cf. 3.2.4) can migrate through compacted bentonite. However, according to results by Maes et al. (2006, 2011), actinide transport by natural organic matter through clay pore systems is limited because the competing dissociation of the organic actinide complexes results in the release of the actinides from the humics and their almost immediate adsorption onto the solid phase which reduces transport (the humics move but the actinides are retained). Similar questions arise for the An(IV)-silica colloids described in 3.1.2 which carry negative charge at near-neutral pH and typically have molecular weights between 10 and 300 kDa (cf. Dreissig et al., 2011). If such particles should be formed in the near-field of nuclear waste repositories, nothing is known about

their migration through compacted bentonite clay, Boom Clay, Opalinus Clay, cement, fractured rock, etc. Diffusion studies for An(IV)-silica nanoparticles and An(IV)-hydroxy aluminosilicate nanoparticles through clays and other geomaterials are needed. The same holds for low organic molecular weight organic acid based nanoparticles (cf. 3.1.4). Another problem which needs further elucidation is that also the immobilizing effect of increased ionic strength may be questionable for some sorts of colloids since certain An(IV) colloids (An(IV) oxyhydroxide colloids) seem to be stable regardless of ionic strength (cf. 3.1.1).

In the far-field of a nuclear waste repository or at other actinide(IV)-contaminated sites such as those described in Section 4, items (ii) and (iii), i.e. colloid-chemical stability and chemical stability of the An(IV) colloids, are the most important criteria for actinide(IV) migration. It is obvious that aggregation, settlement and adsorption will immobilize colloid-borne An(IV). But also the disintegration of the particles by An(IV) desorption from the colloids or by complete particle dissolution will immobilize the tetravalent actinides since the actinides readily adsorb onto the solid phase after release from the colloids (cf. 2.3).

There are still significant knowledge gaps regarding the formation and behavior of An(IV) colloids. In the following we give some of the issues on which future work should focus.

- (a) Formation, exact chemical composition, size and internal structure of the relatively simple An(IV) oxyhydroxide, An(IV)-silica and An(IV)-hydroxy aluminosilicate colloids, which might be precursors of more complex colloids (cf. Schäfer et al., 2012), should be further elucidated. Soft ionization methods such as ESI mass spectrometry and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (cf. Walther and Denecke, 2013), X-ray photoelectron spectroscopy (XPS), neutron scattering, nuclear magnetic resonance (NMR) spectroscopy and synchrotron-based X-ray spectroscopy methods such as EXAFS spectroscopy or high-energy X-ray scattering (HEXS) (cf. Hennig et al., 2013) could be helpful here.
- (b) The nature and the properties of more complex An(IV) nanoparticles such as humic-related, iron oxide-related, waste-form related, cement-related and biological colloids of tetravalent actinides should be further investigated.
- (c) Diffusion, convection and filtration of An(IV) colloids in geo-matrices such as compacted bentonite buffer/backfill material, etc. should be studied more thoroughly (cf. Kurosawa and Ueta, 2001; Voegelin and Kretzschmar, 2002; Wold and Eriksen, 2003; Wold and Eriksen, 2007).
- (d) The type and degree of stabilization of the various An(IV) colloids in the waterborne state (DLVO vs. non-DLVO forces, critical coagulation concentrations of electrolytes, humic/fulvic acid coating of the colloids, etc.) should be identified (cf. Missana and Adell, 2000; Missana et al., 2004; Zänker et al., 2013). The focus should be on stabilization/destabilization at high ionic strength and during sudden decrease of ionic strength (scenarios “shear zone near-field/far-field” and “glacial melt water intrusion”).

³ It is obvious that in ultrapure water An(IV) oxyhydroxide colloids is the only type of colloids that can form. However, environmental waters are not ultrapure but contain, for instance, dissolved silicic acid at concentrations of about 10^{-5} M to 10^{-3} M (Siever, 1972), i.e. they possess Si concentrations much higher than the actinide concentrations normally expected. In studies on 10^{-10} M to 10^{-8} M Th(IV) traces added to real groundwaters (Gorleben waters) to simulate An(IV) behavior in natural water Lieser and Hill (1992) found that the reaction of Th with silicic acid (formation of Th(IV)-silica colloids) is by many orders of magnitude preferred over the interaction of the hydroxo complexes of Th with each other (formation of Th(IV) oxyhydroxide colloids).

Table 1

Types of An(IV) colloids and evidence of their occurrence in real samples.

Type of colloid	Formation in lab experiments	Occurrence in natural samples or field experiments	Sections in this article
<i>Colloids containing structural An(IV)</i>			
An(IV) oxyhydroxide colloids	Proved	Postulated	3.1.1, 4.3
An(IV)-silica colloids	Proved	Postulated	3.1.2, 3.2.8
An(IV)-hydroxy aluminosilicate colloids	Hypothesized	Hypothesized	3.1.3, 3.2.8
An(IV) clusters due to low MW organic acids	Proved	Hypothesized	3.1.4
<i>Colloids carrying adsorbed An(IV)</i>			
An(IV)-clay mineral colloids	Proved	Proved	3.2.1, 3.2.8, 4.2
An(IV)-iron oxide colloids	Proved	Proved	3.2.2, 4.3
An(IV) colloids due to sorption onto silica particles	Proved	Postulated	3.2.3
An(IV)-humic colloids	Proved	Proved	3.2.4, 4.2, 4.3, 4.4
Humic substance stabilized inorganic colloids containing An(IV)	Proved	Proved	3.2.5
Further An(IV)-NOM colloids	Proved	Proved	3.2.6
An(IV) biocolloids	Proved	Proved	3.2.7
An(IV) colloids due to waste form corrosion	Proved	Postulated	3.2.8
An(IV) colloids from cementitious systems	Proved	Postulated	3.2.9

(e) The chemical stability of the various An(IV) colloids (resistance to particle dissolution or An(IV) desorption from the particles) should be determined.

Answering these questions will help to develop better models for describing the colloid-facilitated transport of tetravalent actinides in the environment. This will ease the scientific interpretation of (past and future) real-world scenarios of An(IV) migration and the performance assessment of nuclear waste repositories.

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